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(54) **Polymeric films**

Kunststofffilme

Films polymères

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(56) References cited:
EP-A- 0 083 495
EP-A- 0 312 226
EP-A- 0 312 289
EP-A- 0 545 650
EP-A- 0 546 741
US-A- 4 560 614

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Description

This invention concerns polymeric films and especially polymeric films for producing labels.

The use of polymeric films to produce labels has been increasing in recent years. Labels produced from polymeric films have a number of advantages, for example compared with paper labels. In particular labels produced from polymeric films can be applied to articles by the so-called in-mold labelling technique in which a preformed and usually pre-printed polymeric film label is introduced into a mold prior to the article being molded in the mold, for example by injection molding or blow molding, so that the label forms an integral part of the surface of the article.

Self-adhesive labels produced from polymeric films have also found wide acceptance, such labels often being presented on a strip of material having a release surface from which the labels can be peeled as required.

A number of proposals have been made hitherto for the types of polymeric films which can be used to form labels, biaxially oriented films based on propylene polymers having found wide acceptance for the purpose due to their inherent properties, for example stiffness combined with printability and the ability to adhere to molded polypropylene articles during in-mold labels can be transparent or opaque, as desired.

An example of a hitherto proposed opaque polypropylene film for use in producing labels consists of a relatively thick core layer of a voided propylene homopolymer with relatively thin layers of a non-voided polymer on either side of the core layer, voiding of the core having been achieved by biaxially stretching the film with a phase-distinct particulate material, e.g. chalk, in the core layer. The voids in the core provide these films with opacity, and the non-voided outer layers provide them with printability and/or the ability to adhere to articles as the articles are being molded. Such films are in essence identical to packaging films as are proposed, for example, in EP0004633-A, but they will usually be used at considerably greater thicknesses. Thus whereas packaging films are often used at thicknesses of about 30µm, films used for labelling are often in excess of 50µm thick in order to achieve the desired stiffness to facilitate application of the labels to articles which are to be labelled.

Although the use of a voiding agent does impart opacity to voided films, the films are often not sufficiently opaque for some end uses, for example in-mold labels on highly opaque articles where it is desired that the background of a printed label should merge into the surface of the labelled article so that the edged of the label is difficult if not impossible to see with the naked eye. This has led to the use of highly opaque fillers, and especially titanium dioxide, the particle size of the titanium dioxide generally being too small to effect voiding.

In order to provide voided polypropylene films with high surface gloss, it has been proposed hitherto to use not only an outer, non-voided printable layer, but a further non-voided layer, for example of a propylene homopolymer, between the outer layer and the voided core. It is believed that this non-voided layer improves the surface gloss of the films by masking the effect of the surface irregularities on the voided layer caused by the voiding agent disrupting the surface of the voided layer. However, although the surface gloss of a voided film can be improved by such a technique, the films have inadequate opacity for many end uses.

EP0546741-A describes biaxially oriented films for in-mold labelling which consist of a pigmented, non-voided polypropylene core layer with a layer of voided polypropylene on one surface and a printable layer on its other surface.

Biaxially oriented films having puncture resistance and consisting of a voided core layer of polypropylene with a layer of non-voided polypropylene and an outer layer of a heat sealable polymer on one side and at least one non-voided layer on the other surface of the core are described in EP0545650-A.

EP312226-A describes films with good gloss and printability having a core layer of polypropylene, a layer of voided polypropylene being on one side of the core and a layer of a printable polymer on the other.

Opaque, biaxially oriented films with a voided core layer and two outer skin layers are described in EP0083495-A, the void initiating particles being spherical.

Biaxially oriented polypropylene films which have been surface treated to enhance wettability, and include talc and optionally titanium dioxide to prevent film blocking, are described in US4560614-A.

According to the present invention there is provided a biaxially oriented polypropylene film comprising a core layer of voided polypropylene homopolymer with a layer of non-voided polypropylene homopolymer on one surface thereof and an outer, printable layer of a polyolefin containing units derived from two or more of ethylene, propylene, but-1-ene and higher alpha-olefins on the non-voided polypropylene homopolymer layer, and the surface of the core layer opposite to the non-voided layer having at least one further polymeric layer thereon the outer surface of which being matt and comprising a blend of incompatible polymers, the core layer and/or the said non-voided layer including titanium dioxide.

The titanium dioxide can be present in the non-voided layer and not in the core layer, in the core layer and not in the non-voided layer, or it can be present in both layers. It has, however, been surprisingly found that particularly high opacity can be achieved by the titanium dioxide being present in only one of these layers. Furthermore, the use of a voided core layer enables films of the present invention to be produced having densities in the range of from 0.55 to 0.80 despite the presence of the titanium dioxide, thereby giving a high yield of film for a given amount of polymer combined

with high opacity.

The amount of titanium dioxide used in the layer or layers in which it is present should be sufficient to impart the desired level of opacity. In general this can be achieved by the use of up to 20 percent of titanium dioxide based on the weight of the particular layer in which it is present, and preferably in the range of from 3 to 15 percent by weight of such layers.

It should also be appreciated that high surface gloss can be achieved with such films whether the titanium dioxide is present in the core layer or the non-voided layer.

The outer printable layer is of a polyolefin containing units derived from two or more of ethylene, propylene, but-1-ene and higher alpha-olefins. The printability of such layers can be increased by known methods, for example by corona discharge treatment or flame treatment.

The surface of the core layer of films of the present invention opposite that having the non-voided layer and the outer, printable layer has at least one further polymeric layer thereon, the outer surface of this layer or layers being matt. The use of a matt surface reduces blocking of the printable layer thereto, thereby reducing the tendency of labels produced from such films to stick together when one is drawn from a stack of labels, for example by suction on the printable surface of the labels.

A matt surface is achieved by the use of a blend of incompatible polymers which form separate phases when mixed. Examples of such blends are described for the writeable layers of films described and claimed in EP0312289-A.

The matt layer will usually be at least 1.5µm thick, although it is generally preferred that such further layers should be not more than 5µm thick, a preferred thickness range being from 2 to 5µm. As will be appreciated, as the thickness of the further layer(s) is increased, the degree of voiding of the core required to produce a film with a particular density will have to be increased.

In another preferred embodiment of the present invention, the matt surface has a low heat seal threshold. By selecting the polymers of this heat sealable layer, films of the present invention can be applied to articles during molding operations using lower temperatures than are used in injection molding, thereby achieving good adhesion to the articles without the use of a hot melt adhesive or a lacquer. Such layers are preferably from 0.2 to 2.0µm thick.

Films of the present invention are particularly preferred for use in the production of labels. They therefore preferably have a thickness of from 60 to 90µm, and with advantage for in-mold labelling of injection moldings a thickness of about 80µm, whereas when they have a low heat seal threshold they preferably have a thickness of about 70µm.

The thickness of the non-voided layer between the core layer and the printable layer is preferably from 3 to 10µm, and the thickness of the outer, printable layer is preferably from 0.5 to 2µm.

The core layer of voided propylene homopolymer will usually represent the balance of the total film thickness, although as will be appreciated this will not be the case if other, optional layers are present, for example between the core layer and either a matt or low heat seal threshold further layer.

Films in accordance with the present invention can be produced by known methods, it generally being preferred to coextrude melts of the polymers for the respective layers through slot dies to form a multi-layer polymer web which is then sequentially stretched. Subsequently, one or both outer surfaces of the films can be treated to increase their surface energy, for example by corona discharge treatment or flame treatment.

Films in accordance with the present invention can, if desired, include one or more additives in one or more of the layers, for example anti-block agents, antistatic agents, anti-oxidants and slip agents.

The following Example is given by way of illustration only. All melt flow index values are measured under ASTM D 1238/73 (condition L).

Example

A four-layer polymeric web was produced by coextruding through a slot die a layer of substantially isotactic propylene homopolymer containing 9 percent by weight of calcium carbonate of 3.5µm mean particle size with a blend of 32.5 percent by weight of polyethylene having a melt flow index of 0.12 g/10 min and 67.5 percent by weight of a copolymer of ethylene and propylene (4 percent units derived from ethylene) having a melt flow index of 8 g/10 min on one side and on the other side a layer of substantially isotactic polypropylene homopolymer containing 14 percent by weight of titanium dioxide and an outer layer of a propylene/ethylene copolymer containing 4 percent by weight of units derived from ethylene.

The resulting web was cooled on a chill roller and then heated by passing it over heated rollers rotating at different peripheral speeds to effect stretching of the web in the direction of extrusion. Thereafter the web was stretched in the transverse direction whilst heating the web in a stenter oven.

The biaxially stretched film produced was then cooled, corona discharge treated on both surfaces, and wound up.

The film had a total thickness of 80µm, the layer of the polymer blend being 4µm, the layer of titanium dioxide-containing homopolymer being 8µm, and the outer layer of the propylene/ ethylene copolymer being 1µm. The layer of homopolymer containing the calcium carbonate had developed voids as a result of the stretching and it formed the balance of the total film thickness. The film had a density of 0.62.

The film had high opacity and following printing of

the printable surface, cutting into labels and stacking for in-mold labelling, the individual labels separated well from each other when removed from the stack by the application of suction to the printed surface. The labels also behaved satisfactorily when applied as an in-mold label to an injection molded pot.

The labels could also be removed individually from the stack by sliding.

Claims

1. A biaxially oriented polypropylene film comprising a core layer of voided polypropylene homopolymer with a layer of non-voided polypropylene homopolymer on one surface thereof and an outer, printable layer of a polyolefin containing units derived from two or more of ethylene, propylene, but-1-ene and higher alpha-olefins on the non-voided polypropylene homopolymer layer, and the surface of the core layer opposite to the non-voided layer having at least one further polymeric layer thereon the outer surface of which being matt and comprising a blend of incompatible polymers, the core layer and/or the said non-voided layer including titanium dioxide.

2. A film according to claim 1, wherein the core layer contains titanium dioxide and the said non-voided layer is substantially free of titanium dioxide.

3. A film according to claim 1, wherein the said non-voided layer contains titanium dioxide and the core layer is substantially free of titanium dioxide.

4. A film according to any of the preceding claims, wherein the titanium dioxide is present in the layer or layers in which it is present in an amount of up to 20 percent by weight of the layer in which it is present.

5. A film according to claim 4, wherein the titanium dioxide is present in an amount of from 3 to 15 percent by weight of the layer in which it is present.

6. A film according to any of the preceding claims, wherein at least one outer surface has been treated to increase the surface energy thereof.

Patentansprüche

1. Biaxial orientierte Polypropylenfolie, **gekennzeichnet durch** eine Innenschicht aus Vakuolen enthaltendem Polypropylen-Homopolymer, mit einer Schicht aus vakuolenfreiem Polypropylen-Homopolymer auf der einen Oberfläche, und einer bedruckbaren Außenschicht auf der vakuolenfreien Polypropylen-Homopolymerschicht aus einem Polyolefin, das Einheiten enthält, die sich von zwei oder mehr Stoffen der Verbindungen Ethylen, Propylen, But-1-en und höheren α-Olefinen herleiten, wobei sich auf der der vakuolenfreien Schicht gegenüberliegenden Oberfläche der Innenschicht noch mindestens eine weitere Polymerschicht befindet, deren Außenoberfläche matt ist und eine Mischung von inkompatiblen Polymeren umfaßt, und die Innenschicht und/oder die vakuolenfreie Schicht Titandioxid enthält.

2. Folie nach Anspruch 1, **dadurch gekennzeichnet**, daß die Innenschicht Titandioxid enthält und die vakuolenfreie Schicht im wesentlichen frei von Titandioxid ist.

3. Folie nach Anspruch 1, **dadurch gekennzeichnet**, daß die vakuolenfreie Schicht Titandioxid enthält und die Innenschicht im wesentlichen frei von Titandioxid ist.

4. Folie nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, daß das Titandioxid in der Schicht oder in den Schichten, in denen es vorhanden ist, in einer Menge bis zu 20 Gew% in der Schicht vorliegt, in der es vorhanden ist.

5. Folie nach Anspruch 4, **dadurch gekennzeichnet**, daß das Titandioxid in einer Menge von 3 - 15 Gew% in der Schicht vorliegt, in der es vorhanden ist.

6. Folie nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, daß mindestens eine der Außenoberflächen einer Behandlung zur Erhöhung ihrer Oberflächenenergie unterzogen worden ist.

Revendications

1. Film de polypropylène à orientation biaxiale, comprenant une couche de coeur en un homopolymère polypropylène comportant des vides, avec sur l'une de ses surfaces une couche d'un homopolymère polypropylène sans vides, et, sur la couche homopolymère polypropylène sans vides, une couche imprimable extérieure d'une polyoléfine contenant des motifs dérivant de deux ou plus de deux oléfines parmi l'éthylène, le propylène, le but-1-ène et les alpha-oléfines supérieures, et la surface de la couche de coeur opposée à la couche sans vides étant revêtue d'au moins une autre couche polymère, dont la surface extérieure est mate et comprend un mélange de polymères incompatibles, la couche de coeur et/ou ladite couche sans vides comprenant du dioxyde de titane.

2. Film selon la revendication 1, dans lequel la couche de coeur contient du dioxyde de titane et ladite couche sans vides est pratiquement exempte de

dioxyde de titane.

3. Film selon la revendication 1, dans lequel ladite couche sans vides contient du dioxyde de titane, et la couche de coeur est pratiquement exempte de dioxyde de titane.

4. Film selon l'une quelconque des revendications précédentes, dans lequel le dioxyde de titane est présent dans la ou les couches dans lesquelles il est présent, en une quantité allant jusqu'à 20 % en poids par rapport à la couche dans laquelle il est présent.

5. Film selon la revendication 4, dans lequel le dioxyde de titane est présent en une quantité de 3 à 15 % en poids par rapport à la couche dans laquelle il est présent.

6. Film selon l'une quelconque des revendications précédentes, dans lequel au moins une surface extérieure a été traitée pour en augmenter l'énergie superficielle.